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# Synthesis of (Silylamino)phosphines By The Wilburn Method

by

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Experimental details for the large scale (1-2 mol) synthesis of (silylamino)phosphines by the Wilburn method are described. In a "one-pot" procedure, treatment of $PCl_3$ with one equivalent of $LiN(SiMe_3)_2$ in $Et_2O$ at -78°C followed by two equivalents of RMgX at 0°C affords 67-75% yields of $(Me_3Si)_2NPR_2$

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Contribution from the
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# SYNTHESIS OF (SILYLAMINO)PHOSPHINES BY THE WILBURN METHOD

Robert H. Neilson and Patty Wisian-Neilson

(Dedicated to the memory of Dr. James C. Wilburn, 1953 - 1981)

Received _____

The importance of (silylamino)phosphines, e.g. $(Me_3Si)_2NPMe_2$, as reagents for the synthesis of organo-substituted phosphazene polymers[1] and other novel organophosphorus compounds[2,3] is now well established. Interest in these and related Si-N-P compounds as ligands in organometallic complexes[4] is also developing and many other synthetic applications are likely to follow.

Most (silylamino)phosphines are prepared from commercially available reagents by a simple "one pot" synthesis first utilized by Wilburn.[5,6] In earlier papers[4a,6] we have described the preparation of a few specific compounds on relatively small scales (50-100 mmol). Because of the synthetic value of these reagents, however, we report here the complete details for the convenient, large-scale (ca. 1-2 mol) synthesis of (silylamino)phosphines via the Wilburn procedure.

## Experimental Section

Materials and General Procedures. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen. Ethyl ether was distilled from calcium hydride prior to use. The

following reagents were obtained from commercial sources: $PCl_3$, $PhPCl_2$, $(Me_3Si)_2NH$, n-BuLi, MeMgBr, and EtMgBr. The silylmethyl Grignard $Me_3SiCH_2MgCl$ was prepared as needed according to the published procedure.[7]

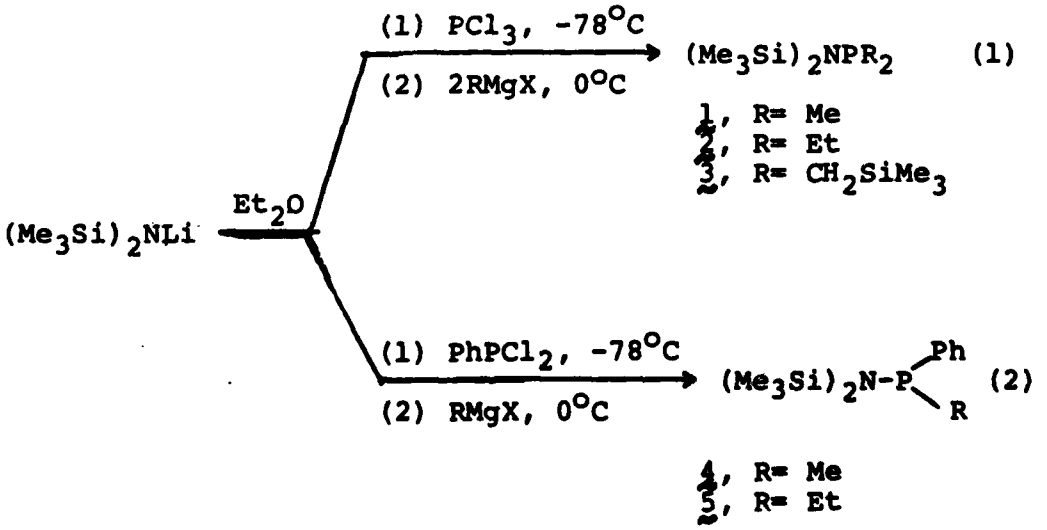
Preparation of [Bis(trimethylsilyl)amino]dimethylphosphine (1). A 5-L, 3-necked flask equipped with a paddle stirrer, a $N_2$-flow, and a 500-mL addition funnel was charged with $(Me_3Si)_2NH$ (1.0 mol, 209 mL) and $Et_2O$ (ca. 1.0 L). One bottle of n-BuLi (ca. 1.0 mol, 2.0 M in hexane) was transferred to the addition funnel under nitrogen pressure by means of a flexible, double-ended syringe needle[8] and was added dropwise to the stirred silylamine solution at 0°C. The addition funnel was then washed with ca. 30 mL of ether and charged with $PCl_3$ (1.0 mol, 87.2 mL). After stirring the $LiN(SiMe_3)_2$ mixture at room temperature for ca. 90 min, it was cooled to -78°C and the $PCl_3$ was added dropwise. Upon completion of the addition, the -78°C bath was removed. During the warm-up period the orange colored solution gradually turned white as LiCl precipitated. After ca. one hour the mixture was cooled to 0°C and the addition funnel was again rinsed with $Et_2O$. Two bottles of MeMgBr (ca. 2.0 mol, 3.0 M in $Et_2O$) were transferred via the double-ended needle to the addition funnel and added dropwise to the stirred reaction mixture at 0°C over ca. 2 hours. The mixture was stirred for 3 hours and then allowed to stand over night at room temperature. Under a stream of $N_2$, the supernatant solution was decanted into a large 1-necked flask. The solids were washed with two 500-mL portions of $Et_2O$ and the washings were added to the first decantate. Most of the solvent was removed under reduced pressure and ca. 500 mL of hexane was added to facilitate precipitation of the remaining Grignard salts.

Filtration under $N_2$ followed by solvent removal left a viscous orange colored residue. Distillation through a short or semi-short path distilling head gave $(Me_3Si)_2NPMe_2$[5,6] as a colorless liquid (166 g, 75% yield[9], bp 55-60°C/4mm) of high purity based on $^1H$ and $^{31}P$ NMR spectra.

Preparation of Other (Silylamino)phosphines. The same procedure using either commercial EtMgBr or freshly prepared $Me_3SiCH_2MgCl$[7] affords the corresponding dialkylphosphines $(Me_3Si)_2NPR_2$, 2: R=Et[10] and 3: R= $CH_2SiMe_3$.[4a] Alternatively, if $PhPCl_2$ is used in place of $PCl_3$ and one equivalent of an alkyl Grignard is added in the last step, then the alkyl(phenyl)phosphines $(Me_3Si)_2NP(Ph)R$, 4: R= Me[6] and 5: R= Et[10], are obtained.

## Results and Discussion

Treatment of a suspension of lithium bis(trimethylsilyl)amide in ether at -78°C with phosphorus trichloride followed by the addition of two equivalents of an alkyl Grignard reagent at 0°C affords the [bis(trimethylsilyl)amino]dialkylphosphines 1 -3 (eq 1). Similarly, the use of dichlorophenylphosphine and one equivalent of Grignard reagent permits the convenient preparation of the corresponding alkyl(phenyl)phosphines 4, 5 (eq 2). With the exception of



some $^{31}P$ chemical shifts (Table I), the characterization of these compounds has generally been reported in other papers[4a,6] describing their reactivity.

These reactions are easily carried out on large scales (ca. 1-2 mol) using unpurified commercial reagents. The products are obtained in relatively high yields (Table I) and good purity after a single vacuum distillation. Generally, the (silylamino)phosphines are colorless, foul-smelling liquids which are sensitive to oxidation and hydrolysis on exposure to the air. Nevertheless, their thermal stability is satisfactory and they can be stored indefinitely in tightly sealed containers.

This simple, "one-pot" synthesis is actually more general than is indicated here. For example, several different silylamines have been used[5,6] and in favorable cases it is possible to obtain monc-alkylated products, e.g. $(Me_3Si)_2NP(Cl)CH_2SiMe_3$.[4a] In more recent studies[11] involving very sterically congested systems, however, we find that reduced (P-H) or coupled (P-P) products are often obtained. Details of this work will be reported in subsequent papers.

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9. Yields up to 86% have been obtained by more careful and repeated washing of the solids.

10. $^1$H NMR data: 2, $\delta$ 0.34 ($Me_3Si$, $J_{PH}$ = 0.6 Hz), $\delta$ 1.14 ($CH_3$, $J_{PH}$= 16.0 Hz, $J_{HH}$= 7.5 Hz), $\delta$ 1.4-2.0 ($CH_2$, multiplet). 5, $\delta$ 0.25 ($Me_3Si$, $J_{PH}$= 0.6 Hz ), $\delta$ 1.33 ($CH_3$, $J_{PH}$= 18.0 Hz, $J_{HH}$= 7.2 Hz), $\delta$ 1.9-2.2 ($CH_2$, multiplet), $\delta$ 7.1-7.4 (Ph, multiplet)

11. manuscripts in preparation.

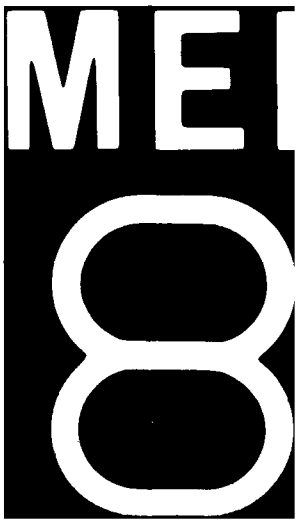
Table I. Physical and $^{31}P$ NMR Data for Some (Silylamino)phosphines, $(Me_3Si)_2NPRR'$

| Compd | R | R' | bp(mm) | Yield (%) | $\delta(^{31}P)$[a] |
|---|---|---|---|---|---|
| 1 | Me | Me | 55-60° (4) | 75 | 31.7 |
| 2 | Et | Et | 68-69° (1.6) | 71 | 57.2 |
| 3 | $CH_2SiMe_3$ | $CH_2SiMe_3$ | 80-85° (0.3) | 67 | 42.9 |
| 4 | Me | Ph | 90-95° (0.8) | 81 | 37.6 |
| 5 | Et | Ph | 85-90° (0.1) | 59 | 50.9 |

[a]Chemical shifts downfield from external $H_3PO_4$, measured in $CDCl_3$ solution.


## Abstract

Experimental details for the large scale (1-2 mol) synthesis of (silylamino)phosphines by the Wilburn method are described. In a "one-pot" procedure, treatment of $PCl_3$ with one equivalent of $LiN(SiMe_3)_2$ in $Et_2O$ at -78°C followed by two equivalents of RMgX at 0°C affords 67-75% yields of $(Me_3Si)_2NPR_2$ (R = Me, Et, $CH_2SiMe_3$). Similarly, $(Me_3Si)_2NP(Ph)R$ (R = Me,Et) are obtained in 59-81% yields starting from $PhPCl_2$. Physical and $^{31}P$ NMR data for these compounds are reported along with references to earlier papers describing their derivative chemistry.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